Supporting Information

for

Coverage-Dependence of Methanol Dissociation on TiO$_2$(110)

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Fitting procedure of the SFG vibrational spectra

The SFG intensity is given by

$$I_{SFG} \propto \left| A_{NR} + \sum_q \frac{A_q e^{i\Phi_q}}{\omega_{IR} - \omega_q + i\Gamma_q} \right|^2 I_{Vis}I_{IR} \propto N^2|\beta|^2 \tag{S1}$$

where A_{NR} is nonresonance amplitude; A_q, Φ_q, ω_q, Γ_q are the resonant amplitude, phase, frequency and damping constant (half width at half maximum) of the q-th mode, respectively; N is the number density of adsorbates; β is the second-order molecular hyperpolarizability, which is proportional to the IR and Raman transition moments of vibration modes. All the SFG spectra were normalized to the SFG generated from the bare $TiO_2(110)$ surface by flashing at 700 K to remove absorbed species on the surface.

For a Lorentzian line, the peak area is proportional to A_q^2/Γ. So the number density of adsorbates N can be obtained from

$$N \propto A_q/\sqrt{\Gamma} \tag{S2}$$

The strong power of focused probing laser could possibly affect the adsorbates state, like multiple photon absorption, local heating and so on, which are required to be excluded in our measurements. Therefore, power-dependent *ssp* SFG on 1 layer CH_3OH on $TiO_2(110)$ was performed by reducing both visible and IR power. As illustrated in Figure S2, within the error of measurements, probing laser didn't affect the adsorption state of CH_3OH.
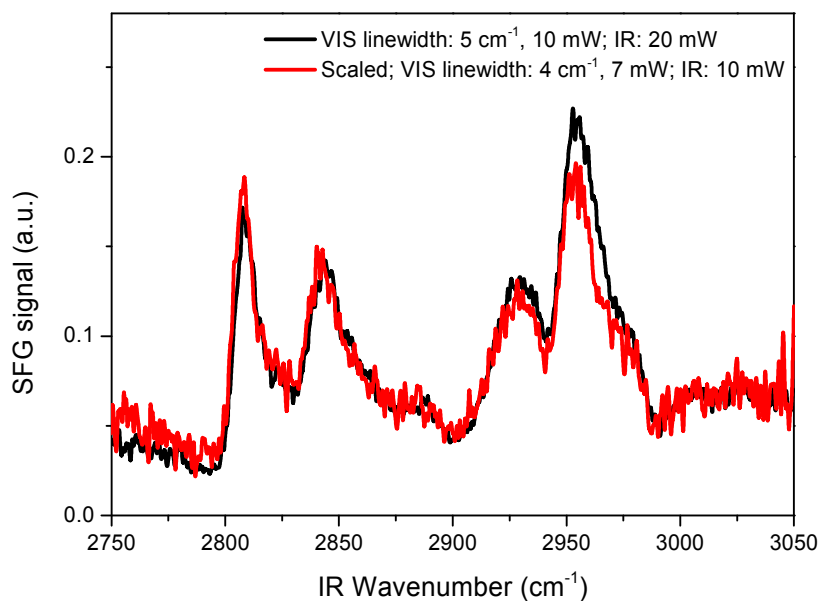

Figure S1. Power-dependent *ssp* SFG measurements of 1 layer CH_3OH on TiO_2 (110). The black curve corresponds to visible silt set as 0.4 mm (line width 5.5 cm^{-1}, 10 mW) and IR power at about 20 mW, and the red curve corresponds to visible slit set as 0.3 mm (line width 4.5 cm^{-1}, 7.5 mW) and IR power at about 10 mW reduced by a silicon plate at 0° incidence.
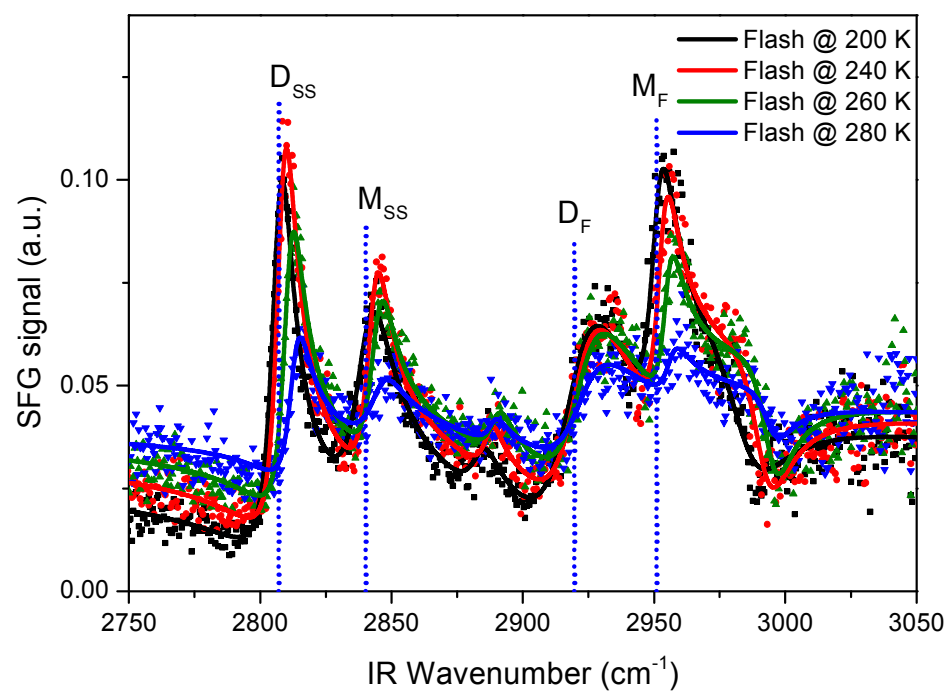
Figure S2. Replotting of Figure 1 for showing a clearer trend of nonresonance. Obviously, the nonresonance becomes stronger when the sample was flashed at higher temperature, which leads to less adsorbates on the surface.
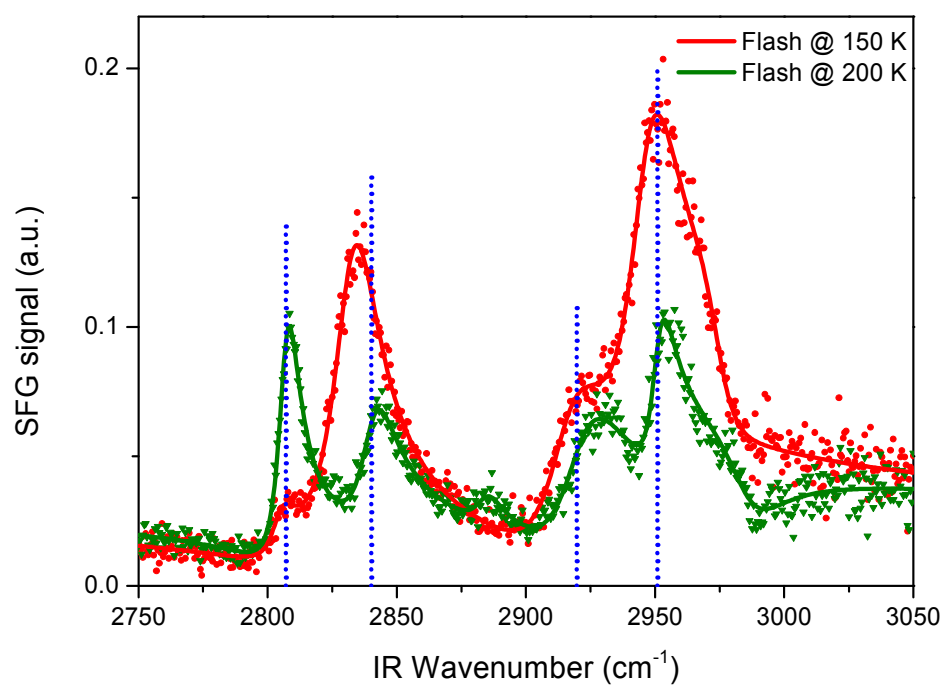
Figure S3. Replotting of the SFG spectra in Figure 4 with flashing temperature of 150 K and 200 K to compare the peak at about 2890 cm^{-1}.

Table S1. The fitting results of SFG spectra in Figure 1 and 3. Fitting errors are shown with 95% confidence level. Some phases for different spectra were set as the same in the fitting. The spectra for 140 K is complicated, so some values were set as fixed, and some fitting values reach the setting bound.

	280 K	260 K	240 K	200 K	160 K	150 K	140 K
A_{NR}	0.28 ± 0.002	0.28 ± 0.003	0.26 ± 0.003	0.24 ± 0.005	0.25 ± 0.01	0.24 ± 0.01	0.23 ± 0.004
A_1	0.58 ± 0.08	1.01 ± 0.07	1.33 ± 0.08	1.43 ± 0.09	0.89 ± 0.26	0.45 ± 0.31	--
A_2	0.43 ± 0.12	0.65 ± 0.08	0.84 ± 0.09	1.27 ± 0.15	2.60 ± 0.29	3.81 ± 0.28	6.34 ± 0.06
A_3	0.10 ± 0.08	0.19 ± 0.10	0.19 ± 0.10	0.26 ± 0.13	--	--	--
A_4	1.09 ± 0.19	1.55 ± 0.20	1.94 ± 0.24	2.71 ± 0.34	2.84 ± 0.54	2.66 ± 0.62	7.4 ± 0.25
A_5	0.20 ± 0.10	0.42 ± 0.08	0.68 ± 0.10	0.87 ± 0.12	2.07 ± 0.38	3.55 ± 0.64	4.44 ± 0.28
A_6	0.21 ± 0.08	0.60 ± 0.10	0.89 ± 0.14	1.10 ± 0.25	0.96 ± 0.45	1.00 ± 0.39	0.24 ± 0.04
Φ_1	0.48 ± 0.05				6.20 ± 0.20		--
Φ_2	0.60 ± 0.09				0.74 ± 0.10	0.56 ± 0.07	0.6 (fixed)
Φ_3	1.09 ± 0.39				--	--	--
Φ_4	0.18 ± 0.12				0.10 ± 0.16		4.97 ± 0.06
Φ_5	0.41 ± 0.12				0.84 ± 0.19	0.54 ± 0.18	6.15 ± 0.09
Φ_6	4.13 ± 0.10				3.93 ± 0.37	3.20 ± 0.31	5.58 ± 0.31
ω_1 (cm^{-1})	2813.0 ± 1.7	2811.0 ± 0.7	2808.5 ± 0.6	2807.1 ± 0.3	2804.2 ± 1.0	2804.0 ± 1.75	--
ω_2 (cm^{-1})	2845.1 ± 0.8	2844.5 ± 0.8	2843.2 ± 0.8	2840.5 ± 0.8	2836.1± 0.9	2832.1 ± 0.5	2831.3 ± 0.1
ω_3 (cm^{-1})	2890.4 ± 3.2	2891.1 ± 2.5	2888.7 ± 2.2	2885.5 ± 2.6	--	--	--
ω_4 (cm^{-1})	2923.2 ± 1.9	2923.0 ± 1.5	2921.9 ± 1.4	2920.4 ± 1.4	2916.8 ± 1.9	2915.0 ± 1.75	2901.4 ± 3.7
ω_5 (cm^{-1})	2955.9 ± 1.8	2954.9 ± 0.7	2952.8 ± 0.6	2950.8 ± 0.6	2950.8± 1.0	2946.2 ± 1.2	2942.8 ± 0.3

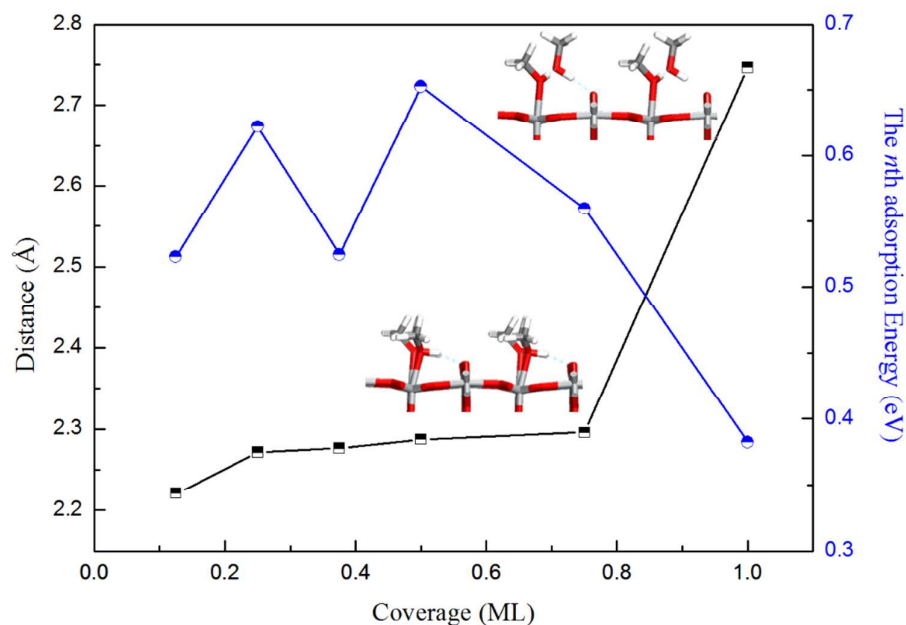| ω_6 (cm^{-1})	2997.6 ± 1.7	2994.9 ± 1.1	2992.0 ± 1.2	2986.0 ± 1.7	2980.8 ± 3.9	2974.0 ± 2.5	2961.6± 0.92
Γ_1 (cm^{-1})	5.1 ± 0.9	4.9 ± 0.4	4.8 ± 0.3	5.0 ± 0.3	5.4 ± 1.0	5.7 ± 2.8	--
Γ_2 (cm^{-1})	8.7 ± 2.8	5.7 ± 0.9	5.6 ± 0.7	8.4 ± 1.0	11.3 ± 1.0	11.2 ± 0.7	5.1 ± 0.1
Γ_3 (cm^{-1})	4.5 ± 4.5	5.1 ± 3.0	4.5 ± 2.6	5.8 ± 3.2	--	--	--
Γ_4 (cm^{-1})	14.3 ± 2.8	13.6 ± 1.9	13.6 ± 1.6	15.5 ± 1.7	15.6 ± 2.2	14.6 ± 2.4	20 (bound)
Γ_5 (cm^{-1})	5.8 ± 3.2	4.6 ± 1.0	5.0 ± 0.7	5.6 ± 0.7	9.0 ± 1.0	12.3 ± 1.3	9.3 ± 0.4
Γ_6 (cm^{-1})	5.4 ± 2.5	6.6 ± 1.4	8.4 ± 1.5	13.0 ± 2.8	12.4 ± 4.3	10.4 ± 2.7	4 (bound)

Figure S4. Relation of the average methanol-surface distance (left Y axis, black line) and the *n*th adsorption energy (right Y axis, blue line) to the methanol coverage. The distance is calculated between the oxygen atom of methanol and the nearest titanium atom on the surface. Atomic structures (stick mode) of 3/4 and 1 ML coverage are shown in the inset.

Figure S4 shows the relation of the average methanol-surface distance and the *n*th adsorption energy to the methanol coverage. At 1/8 ML, the calculated adsorption energy is about 0.52 eV. As increasing the coverage to 1/4 ML, the two methanol prefers to adsorb nearby to form a dimer. The third methanol does not like to stay with the same Ti trough with the previous two because of the repulsion, and it occupies another trough. The fourth one stays beside the third one to form another dimer. The 5th and 6th methanol molecules stay the aforementioned Ti trough, respectively, and the adsorption energy for each methanol is about 0.50 - 0.60 eV.

Table S2. The adsorption energies of different dissociated configurations in Figure S5.

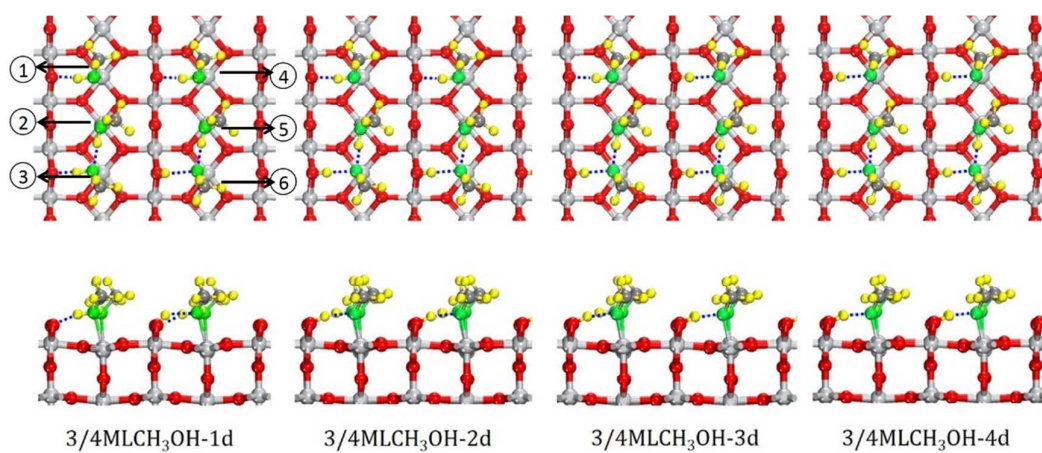| Configurations	Adsorption energy (eV)
3/4 ML CH$_3$OH	0.57
3/4 ML CH$_3$OH-1d	0.55
3/4 ML CH$_3$OH-2d	0.55
3/4 ML CH$_3$OH-3d	0.51
3/4 ML CH$_3$OH-4d	0.47

Figure S5. Top and side views of different adsorption configurations of 3/4 ML methanol in the first layer. Dashed lines represent hydrogen bonds.

Table S3. Polar angles θ of the C_{3v} symmetry axis of the CH_3 group relative to the surface normal [110] and azimuth angles φ relative to the Ti_{5c} row [001] on the surface from the calculation results. The number ①-⑥ indicate the position of methanol or methoxy in Figure S5.

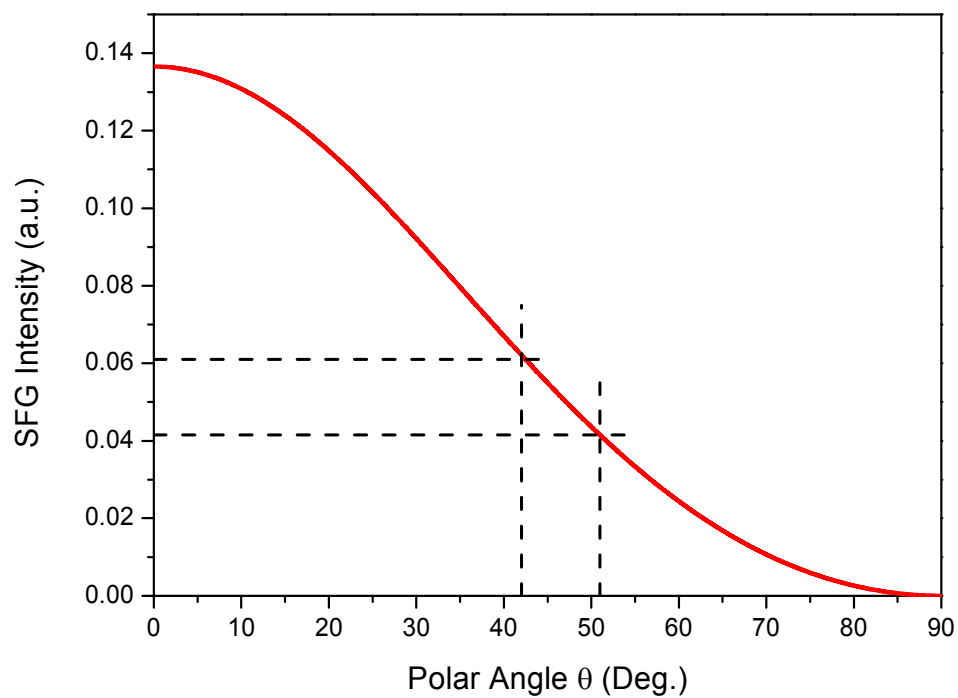| Structure		$C_{3v}\vee[110]$	$C_{3v}\vee[001]$		$C_{3v}\vee[110]$	$C_{3v}\vee[001]$
3/4 ML	①	51.2	15.4	④	50.0	15.6
	②	44.2	64.9	⑤	44.1	65.8
	③	45.7	26.0	⑥	45.0	24.2
3/4 ML-1d	①	51.1	15.2	④	51.2	15.6
	②	44.0	65.0	⑤	43.3	62.0
	③	45.5	26.2	⑥	44.6	30.8
3/4 ML-2d	①	51.0	15.0	④	51.0	15.0
	②	43.1	61.4	⑤	43.1	61.3
	③	44.9	30.0	⑥	45.0	29.7
3/4 ML-3d	①	51.2	16.6	④	48.0	13.7
	②	43.0	62.5	⑤	42.3	60.3
	③	44.2	32.0	⑥	44.0	31.0
3/4 ML-4d	①	47.8	14.7	④	47.7	14.7
	②	42.2	60.3	⑤	42.2	60.3
	③	43.9	31.0	⑥	43.8	30.9

Figure S6. SFG signal in *ssp* polarization combination for ν_s vibrational modes of the CH_3 group against its polar angle. The vertical dashed lines correspond to the polar angle range of CH_3 group at 3/4 ML coverage shown in Figure S5.

In order to know whether the slab is thick enough to represent the methanol adsorption, the adsorption energy of methanol on 4, 6 and 8 layers TiO_2 at the coverage of 1/8 ML were checked, respectively. The dissociated methanol (methoxy) is more stable than the molecular methanol by 0.04 eV, 0.06 eV and 0.06 eV for 4, 6 and 8 layers TiO_2, respectively. Such results suggest that these two states can coexist at the low coverage considering the small energy difference between them. Meanwhile, the 4 layers substrate is thick enough to represent the methanol adsorption states on $TiO_2(110)$ in the current study.

It should be noted that the electronic structure usually is affected by the U value used in the calculations. U=4.2 eV is widely used for the TiO_2 system, which can give the reasonable electronic structure as shown in the previous work.[55, 64] In order to check whether the different U values can affect the relative stabilities between the molecular and dissociate methanol at the coverage of 1/8 ML, the extra calculations with U values of 5 eV and 3 eV were carried out. The calculated results show that the dissociated methanol (methoxy) is more stable than the molecular methanol by 0.07 eV with U=5 eV and by 0.04 eV with U=3 eV, which is close to 0.04 eV with U=4.2 eV. All the results suggest the energy difference between these two states is quite small no matter what U is used, thus the molecular and dissociated states should coexist at the low coverage. In the following, U=4.2 eV is used excepted we noted.